

DESCRIPTION
DEINKING AGENT

Technical Field

The present invention relates to a deinking agent.

Prior art

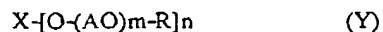
Importance has been increasingly attached to effective use of waste paper in connection with global environment problems such as protection of forest resources and waster disposal. When deinked pulp, which is regenerated from waster paper, is used to attain a high blend ratio thereof, it is necessary to obtain higher-quality deinked pulp, that is, deinked pulp wherein the amount of residual ink is small. For deinking, it is necessary to perform effectively deinking for releasing ink from paper and ink removal for separating the released ink from pulp. About deinking agents, it has been desired to develop deinking agents and ink removing methods which are good in ink releasing property and ink collecting property. As deinking agents, there have been developed a reaction product wherein an alkylene oxide (referred to as an AO hereinafter) is added to a mixture of oil and fat and an alcohol (for example, Japanese Patent No. 1573380), a reaction product wherein an AO is added to an aliphatic acid (for example, Japanese Patent No. 2645208), a reaction product wherein an AO is added to a higher alcohol (for example, Japanese Patent Nos. 2999363 and 3081120), and others. The higher alcohol AO-added

product is used as a deinking agent superior in economy and multiusability.

Disclosure of the Invention

However, the higher alcohol AO-added product has superior ink releasing property, but has strong ink dispersing power so as to be poor in ink collecting property. In order to obtain deinked pulp having a high quality, that is, having a little remaining ink, there are measures for using an ink collecting agent, such as an aliphatic acid, together in flotation step and steps previous thereto in order to compensate for ink collecting property; or for allowing a fall in the yield of pulp so as to increase foaming property in flotation step, thereby increasing discharged-froth amount. However, these measures have problems from the viewpoints of workability, facilities, and costs since additional treatment is conducted. It is therefore desired that the performance of deinking agents themselves is made better.

The invention provides a deinking agent comprising a compound represented by the following general formula (Y), its hydroxyl value (OHV), saponification value (SV) and acid value (AV) satisfying the following: $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ ranges from 0 to 0.3.

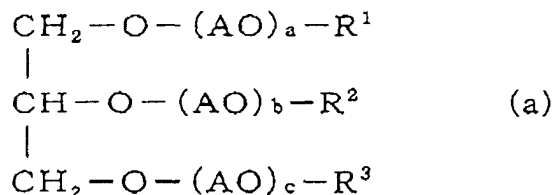


[wherein R is each independently a hydrogen atom or an acyl group having 1 to 24 carbon atoms, provided that at least

one of plural R is an acyl group having 8 to 24 carbon atoms, A is an alkylene group having 2 to 4 carbon atoms, A may be the groups wherein the numbers of their carbon atoms are different, and m x n is a numerical number of from 45 to 1000, X is a polyhydric alcohol group, n is a number of 3 to 10 being equivalent the valence of X.

The term "polyhydric alcohol group" means a residue derived from a polyhydric alcohol by removing hydrogen atoms from alcoholic hydroxy groups thereof.

The present invention relates to a deinking agent comprising a compound represented by the following general formula (a), its hydroxyl value (OHV), saponification value (SV) and acid value (AV) satisfying the following: $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ ranges from 0 to 0.3.



[wherein R^1 to R^3 are each independently a hydrogen atom, or an acyl group having 1 to 24 carbon atoms provided that at least one of R^1 to R^3 is an acyl group having 8 to 24 carbon atoms, A is an alkylene group having 2 to 4 carbon atoms, A may be the groups wherein the numbers of their carbon atoms are different, and $a+b+c$ is a numerical number of from 45 to 1000, preferably from 70 to 1000.]

The present invention also relates to a deinking agent comprising a compound represented by the general formula (a), the hydroxyl value (OHV) of a fraction having a weight average molecular weight of 2000 or more, the saponification value (SV) thereof and the acid value (AV) thereof satisfying the following: $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ ranges from 0 to 0.3.

The present invention also relates to an ink removing method of using the deinking agent of the present invention in an ink removing step.

The invention provides a process for preparing a deinking agent comprising a compound represented by the general formula (Y) as defined above and having the value of $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ in the ranges of from 0 to 0.3 wherein hydroxyl value (OHV), saponification value (SV) and acid value (AV), comprising the step of esterifying an alkylene oxide adduct to a polyhydric alcohol having 3 to 10 valences or a mixture of a polyhydric alcohol having 3 to 10 valences with fats and/or oils with a carboxylic acid at a temperature of 100°C to 260°C.

The invention provides a process for preparing a deinking agent comprising a compound represented by the general formula (Y) as defined above and having the value of $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ in the ranges of from 0 to 0.5 wherein hydroxyl value (OHV), saponification value (SV) and acid value (AV), comprising the step of esterifying an alkylene oxide adduct to a polyhydric alcohol having 3 to 10 valences with a carboxylic acid at a temperature of 100°C to 260°C.

The weight average molecular weight referred to herein

is a molecular weight relative to polystyrene standards, which is measured by gel permeation chromatography (GPC) under the following conditions:

Column: G4000 HXL + G2000 HXL (manufactured by Tosoh Corporation.),

Elution : THF (in 50 mmol/L CH₃COOH),

Flow rate: 1.0 mL/min,

Column temperature: 40°C,

Detector: RI, and

Sample size: 5 mg/mL, 100 µL.

The OHV (hydroxyl value), the SV (saponification value) and the AV (acid value) are measured in accordance with the test methods described in JIS K 0070. Specifically, the OHV, the SV and the AV are measured by potentiometric titration (pyridine-acetic anhydride method), potentiometric titration, and potentiometric titration, respectively.

The compound represented by the general formula (a) is a mixture of compounds having ester bonds and obtained by adding, to glycerin or a mixture of glycerin and oil and fat as starting material, at least one alkylene oxide (referred to as AO hereinafter) selected from ethylene oxide (referred to as EO hereinafter), propylene oxide (referred to as PO hereinafter), and butylene oxide (referred to as BO hereinafter).

According to the present invention described above, provided is a deinking agent comprising an esterified reactant of a reaction product obtained by adding an alkylene oxide having 2 to 4 carbon atoms to glycerin or a mixture of glycerin

and oil and fat, and a carboxylic acid, wherein its hydroxyl value (OHV), saponification value (SV) and acid value (AV) satisfy the following: $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ ranges from 0 to 0.3. The ratio of the compound represented by the general formula (Y) or (a) in the esterification reactants is preferably 80% or more, more preferably 90% or more by weight, and, in particular, the ratio of the compound having a weight average molecular weight of 2000 or more is preferably 80% or more, more preferably 90% or more by weight.

Detailed Description of the Invention

The mechanism that the ink collecting property of the deinking agent of the present invention is good is unclear, but it appears that in the compound represented by the general formula (Y), or preferably (a), in the present invention, micelle structures by linked by AO chains are formed, and the structures contribute to improvement in ink collecting power, as will be described below.

In order to form the micelle structures linked by AO chains, it is preferred that about R of the compound represented by the general formula (Y), preferably R^1 , R^2 and R^3 of the compound represented by the general formula (a), the ratio of acyl groups, which are hydrophobic groups, is large and the ratio of hydroxyl groups, which are hydrophilic groups, is small. In general, in the production of the compound represented by the general formula (Y), preferably (a), there is obtained a mixture of compounds having different numbers of hydroxyl groups or acyl

groups and byproducts having a hydroxyl group, an acyl group and a carboxylic group. The OHV, the SV and the AV are indexes of the number of the hydroxyl groups, the total number of the acyl groups and the carboxylic groups and the number of the carboxylic groups, respectively. As an index of the capability of forming the micelle structures linked by AO chains, the ratio of the hydroxyl groups to the total of the acyl groups ($SV - AV$) and the hydroxyl groups (OHV), $[OHV / (SV - AV + OHV)]$ can be used.

Namely about the compound represented by the general formula (Y) or the general formula (a) in the present invention and contained in the deinking agent wherein the OHV, the SV and the AV satisfy the following: $OHV / (SV - AV + OHV)$ ranges from 0 to 0.3, or 0 to 0.5 in the specified production process, almost all of terminal OH groups of AO chains are substituted with hydrophobic groups. It is therefore considered that, when micelles are formed, one of the two hydrophobic groups of both terminals of the AO chain is taken in hydrophobic moieties of two adjacent micelles. Thus, the AO chain (EO/PO chain or the like) is shared between the hydrophobic groups so that a three-dimensional network structure of the micelles may be formed.

Herein, the ink collecting property is a performance such that ink particles dispersed by the deinking agent are adsorbed on generated bubbles and then float up. The adsorption strength of the dispersed ink particles on the bubbles depends on a hydrophobic bonding strength between the dispersed ink

particles and the bubbles.

About the mechanism of improving the ink collecting power according to the present invention, the following two can be considered:

1) In any (conventional) deinking agent that forms micelles which are not linked by AO chains, it is necessary that its hydrophobic groups adsorbed on ink particles are newly adsorbed on bubbles. However, in the deinking agent of the present invention, hydrophobic groups of micelles which are not adsorbed on ink particles, among micelle structures linked by AO chains, are adsorbed on bubbles and simultaneously ink particles linked by the AO chains are also entrained and adsorbed on this. Thus, the respective hydrophobic groups can independently fulfill their given functions.

2) Since such structures are formed, it is difficult that the ink particles are entirely covered with the hydrophobic groups because of three-dimensional entanglement. It therefore appears that the fact that hydrophobic faces remains in the surfaces of the ink particles is also a factor for promoting adsorption onto the bubbles.

In the deinking agent of the present invention, the $OHV/(SV - AV + OHV)$ is from 0 to 0.3, preferably from 0 to 0.2, and still more preferably from 0 to 0.1. If the $OHV/(SV - AV + OHV)$ is 0.3 or less, the ink collecting power is improved. When compounds having a high OHV value, such as ethylene glycol, glycerin, a lower alcohol having 7 or less carbon atoms, and a low AO molecule added compound, as well as the compound

represented by the general formula (Y) or the general formula (a) are added to the deinking agent, the $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of fractions having a weight average molecular weight of 2000 or more is measured and satisfy the above-mentioned range in order to exclude any effect of the compounds which have a high OHV value and are added afterwards. The foaming property in the step of flotation is decreased so that the yield is improved. The more terminal OH groups of AO chains of the compound of the formula (Y) or (a) are substituted by hydrophobic groups, that is, the closer to zero the value of $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ becomes, the better improved is the compound as defined by the formula (Y) or (a) in collecting power of ink. It is a good deinking agent for a deinking system by which a low foaming is preferred in flotation.

The larger the value of $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ is from zero, on the other hand, the more increased foaming property the compound has. With an increased foaming property the yield rate of pulp is decreased. From the viewpoint of the yield rate of pulp, $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ is preferably not more than 0.5.

From the viewpoint of the foaming property and the yield rate of pulp, $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ ranges preferably from zero to 0.5, more preferably 0.1~0.5, much more preferably 0.2~0.5, especially preferably 0.3 ~ 0.45. $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ is preferably 0.2~0.45 in particularly for a deinking system in which a high foaming property is necessary in flotation and 0.1 ~ 0.3 in particularly for a deinking system in which a low foaming property is necessary.

In production of the compound of the formula (Y) where an alkylene oxide adduct to a mixture of a polyhydric alcohol having 3 to 10 valences with fats and/or oils is esterified with a carboxylic acid, when an alkylene oxide is added to a mixture of the polyhydric alcohol with fats and/or oils, polyalkylene oxide adducts including no polyhydric alcohol is by-produced at the time of esterification or addition of the alkylene oxide. This by-product is poor in deinking. When an alkylene oxide adduct to a mixture of a polyhydric alcohol having 3 to 10 valences with fats and/or oils is used as a raw material for the esterification, $\text{OHV} / (\text{SV} - \text{AV} + \text{OHV})$ is preferably in the range of 0~0.3.

When an alkylene oxide adduct to a polyhydric alcohol having 3 to 10 valences, not mixed with fats and/or oils, is used as a raw material for the esterification, little polyalkylene oxide adducts including no polyhydric alcohol is produced. When an alkylene oxide adduct to a polyhydric alcohol having 3 to 10 valences, not mixed with fats and/or oils, is used as a raw material for the esterification, $\text{OHV} / (\text{SV} - \text{AV} + \text{OHV})$ is preferably in the range of 0~0.5.

The esterification temperature is preferably 100°C to 260°C, more preferably 140°C to 260°C, especially preferably 160°C to 260°C, from the viewpoint of a reaction rate and prevention of cutting of the polyalkylene oxide chain. A suitable catalyst to the reaction temperature may be preferably used.

When a polyhydric alcohol having 3 to 10 valences or a

mixture of a polyhydric alcohol having 3 to 10 valences with fats and/or oils is used as a raw material for the compound (Y), $\text{OHV}/(\text{SV}-\text{AV}+\text{OHV})$ is preferably in the range of 0~0.3.

Particularly preferred is the $\text{OHV} = 0$, namely, the terminal OH groups of AO are completely substituted with hydrophobic groups. It is however allowable that terminal OH groups are partially present.

The average number of the added AO molecules is from 45 to 1000, more preferably from 70 to 1000, still more preferably from 100 to 1000, and particularly preferably from 150 to 1000 per mole of the material to which the AO is to be added. The average number is most preferably from 150 to 600, considering the handling property. If the average number of the added AO molecules is 45 or more, linked micelles are construed to produce the advantageous effects of the present invention satisfactorily.

In the case that two or more (kind) AO are contained in the compound represented by the general formula (Y) or the general formula (a), about the addition form thereof a block polymerization chain or a random polymerization chain is allowable. The form is not particularly limited. Considering an appropriate bubble amount at the time of floatation, about the existence ratio (mole ratio) of EO in the AO the following is preferred: $\text{EO}/\text{AO} = 0.3$ to 1. As the AO, EO and PO are preferably used together. About the mole ratio in this case, $\text{EO}/\text{PO} = 10/0$ to $3/7$ is preferred, and $\text{EO}/\text{PO} = 9/1$ to $4/6$ is more preferred.

R of the general formula (Y) and R^1 to R^3 of the general formula (a) are each a hydrogen atom or an acyl group having 1 to 24 carbon atoms provided that at least one R^1 to R^3 is an acyl group having 8 to 24 carbon atoms. More preferably, two or more thereof are acyl groups. These acyl groups may be unsaturated or saturated. The ratio of acyl groups having 8 to 24 carbon atoms, more preferably 12 to 24 carbon atoms in all groups of R and R^1 to R^3 is preferably 80% or more by weight.

The content of the compound represented by the general formula (Y) or the general formula (a) in the deinking agent is preferably from 50 to 100% by weight, particularly preferably from 70 to 100% by weight.

The compound represented by the general formula (Y) or the general formula (a) can be obtained by esterifying a reaction product wherein the AO is added to glycerin or a mixture of glycerin and oil and fat with a carboxylic acid. The $OHV/(SV - AV + OHV)$ can be adjusted by setting a target value of the AV in light of the mole ratio between charging ingredients, picking up a sample and measuring the AV.

The compound represented by the general formula (a) is also present in a known reaction product wherein an AO is added to a mixture of oil and fat and an alcohol. However, according to this reaction, by-products such as an AO copolymer besides the compound represented by the general formula (a) are produced if they are caused to react in accordance with a formulation described, for example, in Japanese Patent No. 1573380. For this reason, the value of the OHV becomes large so that the

$OHV/(SV + OHV - AV)$ of the whole of the mixture becomes larger than 0.3.

As the carboxylic acid used in the production of the compound represented by the general formula (Y) or the general formula (a), a carboxylic acid having 8 to 24 is used. Specific examples thereof include lauric acid, stearic acid, and oleic acid. If necessary, a carboxylic acid having 1 to 7 carbon atoms can be used together.

The deinking agent of the present invention can be used together with a known deinking agent, for example, a higher-alcohol AO-added product, an aliphatic acid AO-added product, an AO-added product of a mixture of oil and fat and an alcohol, an AO-added product of a mixture of a polyhydric carboxylic acid and an alcohol. The deinking agent of the present invention may be used together with, for example, a higher aliphatic acid, a higher aliphatic acid salt, or the like in order to raise the yield of deinked pulp, and the agent may be used together with sulfate of a higher-alcohol, a polyhydric alcohol such as glycerin, and AO-added products thereof, considering improvement in runnability, such as control of foaming property and antifoaming property in the step of floatation.

Even if the deinking agent of the present invention is added in any step before the step of floatation, higher-quality deinked pulp can be obtained. In general, the deinking agent of the present invention is added in any one of pulping, mixing and flotation steps or in all the steps. The adding amount

thereof is not particularly limited, and is preferably from 0.03 to 1.0% by weight of starting waste paper.

The deinking agent of the present invention makes it possible to improve the ink collecting power in the step of flotation and yield high-quality deinked pulp without lowering the yield of pulp.

Examples

Production Example 1-1

To a 2-liter autoclave were charged 230.3 g of glycerin and 16.8 g of 100% KOH, and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. Next, the reaction mixture was caused to react with 1753 g of a mixture wherein the mole ratio between EO and PO was 228 : 102 (10 moles of EO and 4.5 moles of PO corresponding to one mole of glycerin). About reaction conditions at this time, the temperature was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the temperature was cooled to 80°C to yield an intermediate synthesis product 1 (reactant wherein 10 moles of EO and 4.5 moles of PO corresponded to one mole of glycerin).

Next, 290 g of the intermediate synthesis product 1 was charged into a 2-liter autoclave, and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. The resultant was then caused to react with 1678 g of a mixture wherein the mole ratio between EO and PO was 228 : 102. About reaction conditions at this time, the temperature

was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the temperature was cooled to 80°C to yield an intermediate synthesis product 2 of AV = -1.1, OHV = 35.7 and SV = -1.1 (reactant wherein 76 moles of EO and 34 moles of PO corresponded to one mole of glycerin).

Next, to a 200-mL four-neck flask were charged 124.4 g of the resultant intermediate synthesis product 2 and 26.3 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two (the reaction ratio (a)/(b)), which was calculated from the OHV of the intermediate synthesis product 2 and the AV of stearic acid, would be 1 : 1.2. The mixture was caused to react at 215°C under introduced and sealed nitrogen for 8 hours to yield a synthesis product (the present invention product 7 of Table 1) wherein AV = 6.5, OHV = 2.8, SV = 34.7 and the $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ was 0.09.

Production Example 1-2

To a 2-liter autoclave was charged 668 g of the intermediate synthesis product 2 synthesized in Production Example 1-1, and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. The resultant was then caused to react with 1311 g of a mixture wherein the mole ratio between EO and PO was 228 : 102. About reaction conditions at this time, the temperature was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the temperature was cooled to

80°C to yield an intermediate synthesis product 3 of AV = -0.3, OHV = 16.3 and SV = -0.38 (reactant wherein 228 moles of EO and 102 moles of PO corresponded to one mole of glycerin).

Next, to a 200-mL four-neck flask were charged 136.8 g of the resultant intermediate synthesis product 3 and 13.2 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two, which was calculated from the OHV of the intermediate synthesis product 3 and the AV of stearic acid, would be 1 : 1.2. The mixture was caused to react at 215°C under introduced and sealed nitrogen for 8 hours to yield a synthesis product (No. 1 of Table 1) wherein AV = 2.3, OHV = 0.7, SV = 17.8 and the $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ was 0.04.

Production Example 1-3

To a 2-liter autoclave were charged 151.1 g of tallow, 4.8 g of glycerin (0.3 mole of glycerin per mole of tallow) and 1.2 g of 100% KOH, and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. Next, the reaction mixture was caused to react with 1834.4 g of a mixture wherein the mole ratio between EO and PO was 148 : 66 (148 moles of EO and 66 moles of PO corresponding to one mole of tallow). About reaction conditions at this time, the temperature was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the temperature was cooled to 80°C to yield a synthesis product (reactant wherein 148 moles of EO and 66 moles of PO corresponded to one mole of tallow, No. 17 of Table 1) wherein AV = 0.52, OHV

= 18.9, SV = 16.7 and the $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ was 0.54.

Production Example 1-4

To a 200-mL four-neck flask were charged 134.9 g of the synthesis product synthesized in Production Example 1-3 and 15.1 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two, which was calculated from the OHV of the synthesis product and the AV of stearic acid, would be 1 : 1.2. The mixture was caused to react at 215°C under introduced and sealed nitrogen for 8 hours to yield a synthesis product (No. 14 of Table 1) wherein OHV = 0, and the $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ was 0.

No. 18 of Table 1 was synthesized in the same manner as in Production Example 1-3. About Nos. 2 to 6 and 8 to 13, and Nos. 15 and 16, an AO was added to glycerin in the same manner as in Production Example 1-1 or 1-2 to synthesize, as an intermediate product, a compound before esterifying reaction, and next this intermediate product and a carboxylic acid were charged to conduct esterification.

Table 1

Deinking agent	Intermediate synthesis product (a)			Carboxylic acid(b)	(a)/(b) reaction ratio ^{*1}	OHV/(SV+OHV-AV) ^{*3}
	Starting compound	Average number of added moles of EO/PO	Average number of added moles of AO			
1	Glycerin	EO228/PO102	330	Stearic acid	1/1.2	0.04
2	Glycerin	EO228/PO102	330	Stearic acid	1/1.2	0.12
3	Glycerin	EO228/PO102	330	Stearic acid	1/0.8	0.22
4	Glycerin	EO276/PO124	400	Stearic acid	1/1.2	0.11
5	Glycerin	EO154/PO68	220	Stearic acid	1/1.2	0.11
6	Glycerin	EO114/PO51	165	Stearic acid	1/1.2	0.11
7	Glycerin	EO76/PO34	110	Stearic acid	1/1.2	0.09
8	Glycerin	EO54/PO24	78	Stearic acid	1/1.2	0.08
9	Glycerin	EO38/PO17	55	Stearic acid	1/1.2	0.07
10	Glycerin	EO264/PO66	330	Stearic acid	1/1.2	0.03
11	Glycerin	EO165/PO165	330	Stearic acid	1/1.2	0.02
12	Glycerin	EO228/PO102	330	Lauric acid	1/1.2	0.01
13	Glycerin	EO228/PO102	330	Oleic acid	1/1.2	0.03
14	Tallow/glycerin (molar ratio: 1/0.3)	EO148/PO66	165 ^{*2}	Stearic acid	1/1.2	0.00
15	Glycerin	EO228/PO102	330	Stearic acid	1/0.5	0.52
16	Glycerin	EO28/PO12	40	Stearic acid	1/1.2	0.07
17	Tallow/glycerin (molar ratio: 1/0.3)	EO148/PO66	165 ^{*2}	—	—	0.54
18	Tallow/glycerin (molar ratio: 1/0.3)	EO54/PO27	62 ^{*2}	—	—	0.37
19	Higher alcohol AO-added product [DI-767, manufactured by KAO Corp.]					—

Notes)

*1: Reaction ratio (a)/(b) is a ratio of esterifying reaction, and is represented by the mole ratio between the (a) and the (b), calculated from the OHV of the (a) and the AV of the (b).

*2: The average number of AO molecules added to the glycerin skeleton.

*3: The $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of each deinking agent

Example 1

The deinking agents of Table 1 were used to conduct ink removing treatment and evaluate ink removing performances thereof in accordance with the following steps. The results are shown in Table 2

[Ink removing treatment]

Waste paper collected in a city (starting materials) was deteriorated at 80°C for 5 hours, and cut into 2 cm × 5 cm sizes. Thereafter, a given amount thereof was put into a desk disintegrating machine, and thereto were added hot water, sodium hydroxide in an amount of 0.5% by weight (of the starting materials) and each of the deinking agents in an amount of 0.3% by weight (of the starting materials). The mixture was subjected to disintegrating treatment at a pulp concentration of 4% by weight and at 45°C and 3000 rpm for 10 minutes. Next, the pulp slurry was concentrated up to a pulp concentration of 17% by weight. Thereto were added sodium hydroxide in an amount of 1.0% by weight (of the starting materials), sodium silicate No.

3 in an amount of 2.0% by weight (of the starting materials), hydrogen peroxide in an amount of 0.3% by weight (of the starting materials), and hot water, so as to set the pulp concentration to 15% by weight. In a high temperature water tank of 55°C temperature, the solution was subjected to bleaching treatment for 2 hours. The pulp slurry was diluted with hot water to a concentration of 1.0% by weight. Thereafter, the slurry was subjected to flotation treatment at 40°C for 6 minutes (using a flotater manufactured by Kyokuto Shinko Co., Ltd.).

To the pulp slurry subjected to the flotation was added aluminum sulfate in an amount of 10% by weight of the pulp. After the slurry was stirred, a 150-mesh wire with a 109µm mesh was used to produce a handmade sheet (ink-removed sheet) having a basis weight of 150 g/m² according to JIS P8209.

The pulp slurry obtained by the ink removing treatment was concentrated with a #80 mesh wire with a 180µm mesh so as to have a pulp concentration of 10% by weight. Tap water was used to perform diluting-operation 3 times up to a pulp concentration of 1% by weight. Thereafter, as completely washed pulp slurry, aluminum sulfate in an amount of 10% by weight of the pulp was added, and the resultant was stirred. A 150-mesh wire with a 109µm mesh was then used to produce a handmade sheet (completely washed sheet) having a basis weight of 150 g/m² according to JIS P8209.

[Ink removing performance]

(1) Brightness

About the above-mentioned ink-removed sheet, SPECTRO COLOR METER PF-10 (MGO standard) manufactured by Nippon Denshoku Industries Co., Ltd. was used to measure the brightness by Hunter. The average of values of the front and back surfaces was obtained. A significant difference in the brightness was 0.5% or more in the present example.

(2) Ink collecting property

About the above-mentioned ink-removed sheet and completely washed sheet, ERIC 950 manufactured by Technidyne Corporation. was used to measure the remaining ink effect concentrations. As an index of the ink collecting property, a difference between the remaining ink effect concentration (I) of the completely washed sheet and the remaining ink effect concentration (II) of the ink-removed sheet was used to make evaluation. As the difference is smaller, the ink collecting property is higher. A significant difference is 20 ppm.

(3) Pulp yield

A difference between the weight (A) of the pulp before the ink removing treatment and the weight (B) of the pulp discharged from the upper of the flotater, in the above-mentioned ink removing treatment, was divided by the weight (A) of the pulp before the ink removing treatment, and the resultant value was multiplied by 100 [that is, $[(A)-(B)] \div (A) \times 100$]. The resultant value was defined as the pulp yield (%). A significant difference was 0.5% or more in the present example.

Table 2

Test No. of table I	Brightness (%)	Ink collecting property			Pulp yield (%)
		Remaining ink amount(ppm)		Difference of the (I)from the (O)	
		Completely washed sheet (I)	Ink-removed sheet (O)		
1	50.6	316	644	328	90.7
2	50.1	304	645	341	90.5
3	49.5	310	666	356	90.2
4	50.2	306	638	332	90.2
5	49.9	310	671	361	90.9
6	49.6	305	689	384	91.5
7	49.0	319	732	413	92.2
8	48.8	321	742	421	92.7
9	48.5	318	749	431	93.0
10	50.7	318	639	321	90.2
11	49.7	311	684	373	91.5
12	49.3	324	707	383	90.2
13	49.5	318	698	380	90.3
14	49.3	319	702	383	91.3
20*1	49.7	301	661	360	91.0
21*2	49.6	308	661	353	90.4
15	49.4	321	677	356	86.8
16	47.4	307	873	566	94.8
17	49.3	331	685	354	86.4
18	47.5	329	817	488	90.5
19	47.8	322	786	464	90.5

*1 a mixture of No. 2 and glycerin at 90/10(weight ratio)

*2 a mixture of No. 3 and stearic acid at 95/5(weight ratio)

Production Example 2-1

To a 2-liter autoclave were charged 250.0 g of glycerin and 18.3 g of 100% KOH and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. Next, the reaction mixture was caused to react with 1416 g of a mixture wherein the mole ratio between EO and PO was 210 : 90, corresponding to 7.5 moles of EO and 3.2 moles of PO to one mole of glycerin. About reaction conditions at this time, the temperature was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the mixture was cooled to 80°C. 1434.3 g having been taken out of the autoclave, 250 g remained in the autoclave. The intermediate product of 250 g was, in the autoclave, heated up to 135°C at a stirring rate of about 600 rpm and reacted with 1416 g of a mixture of EP and PO at the mole ratio EP/PO of 210 to 90. About reaction conditions at this time, the temperature was 135°C and the pressure was from 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the mixture was cooled to 80°C. 1166 g having been taken out of the autoclave, 500 g remained in the autoclave. The intermediate product of 500 g, corresponding to 58.7 moles of EO and 25.1 moles of PO to one mole of glycerin, was, in the autoclave, heated up to 135°C at a stirring rate of about 600 rpm and reacted with 1264 g of a mixture of EP and PO at the mole ratio EP/PO of 210 to 90. The reaction conditions were the temperature of 135°C and the pressure of 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the

mixture was cooled to 80°C obtain a reaction product (a1) of AV = -0.13, OHV = 15.2 and SV < 1.

Next, to a one liter four-neck flask were charged 905.9 g of the resultant reaction product (a1) and 88.3 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two (the reaction ratio (a)/(b)), which were calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), would be 1 : 1.3. 0.5 wt.% (5.0g), per the total of the fed reactants, of dibutyl tin oxide as a catalyst was fed and the mixture was reacted for esterification at 225°C \pm 5°C with nitrogen gas blown in.

The synthesis product (No. 1 of Table 3) was obtained by the 4 hour reaction with AV = 5.7, OHV = 3.2, SV = 18.4 and OHV/(SV - AV + OHV) of 0.20.

The synthesis product (No. 2 of Table 3) was obtained by the 5 hour reaction with AV = 5.2, OHV = 2.7, SV = 18.4 and OHV/(SV - AV + OHV) of 0.17.

The synthesis product (No. 3 of Table 3) was obtained by the 6 hour reaction with AV = 4.2, OHV = 1.2, SV = 18.3 and OHV/(SV - AV + OHV) of 0.08.

Production Example 2-2

To a one liter four-neck flask were charged 321.8 g of the reaction product (a1) and 28.9 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two (the reaction ratio (a)/(b)), which were calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), would

be 1 : 1.2. 0.5 wt.% (1.8 g), per the total of the fed reactants, of dibutyl tin oxide as a catalyst was fed and the mixture was reacted for esterification at $215^{\circ}\text{C} \pm 5^{\circ}\text{C}$ with nitrogen gas blown in.

The synthesis product (No. 4 of Table 3) was obtained by the 4 hour reaction with $AV = 8.5$, $OHV = 6.3$, $SV = 17.4$ and $OHV/(SV - AV + OHV)$ of 0.41.

The synthesis product (No. 5 of Table 3) was obtained by the 5 hour reaction with $AV = 7.6$, $OHV = 5.4$, $SV = 17.5$ and $OHV/(SV - AV + OHV)$ of 0.35.

Production Example 2-3

To a 2-liter autoclave were charged 244.2 g of tallow, 5.3 g of glycerin (0.2 mole of glycerin per mole of tallow) and 3.6 g of 100% KOH and then the mixture was heated up to a temperature of 135°C at a stirring rate of about 600 rpm. Next, the reaction mixture was reacted with 1604 g of a mixture of EP and PO having the mole ratio between EO and PO of 206 : 83, corresponding to 69 moles of EO and 28 moles of PO to one mole of glycerin structure. The reaction conditions at this time were the temperature of 135°C and the pressure of 1 to 3 kg/cm^2 (98 to 294 kPa) (gauge pressure). After the end of the reaction, the mixture was cooled to 80°C . 1396 g having been taken out of the autoclave, 460 g remained in the autoclave. The intermediate product of 460 g was, in the autoclave, heated up to 135°C with at a stirring rate of about 600 rpm and reacted with 786 g of a mixture of EP an PO at the mole ratio EP/PO of

206 to 83. The reaction conditions were the temperature of 135°C and the pressure of 1 to 3 kg/cm² (98 to 294 kPa) (gauge pressure). After the end of the reaction, the mixture was cooled to 80°C to obtain a reaction product (No. 19 of Table 3) having AV = 0.06, OHV = 13.8, SV = 8.4 and $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of 0.62, corresponding to 206 moles of EO and 83 moles of PO to one mole of glycerin structure.

Production Example 2-4

To a 200 milliliter four-neck flask were charged 148.0 g of the reaction product (a1) and 22.2 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two (the reaction ratio (a)/(b)), which were calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), would be 1/2. 0.5 wt.% (0.86 g), per the total of the fed reactants, of dibutyl tin oxide as a catalyst was fed and the mixture was reacted for esterification at 215°C ± 5°C with nitrogen gas blown in. The synthesis product was obtained with AV = 14.8, OHV = 2.8, SV = 26.0 and $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of 0.20. Out of this was distilled out stearic acid in vacuum at 5.2 kPa. The synthesis product (No. 6 of Table 3) was obtained with AV = 4.3, OHV = 3.0, SV = 16.3 and $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of 0.20.

Production Example 2-5

To a 200 milliliter four-neck flask were charged 145.4 g of the reaction product (a1) and 13.1 g of stearic acid (AV = 202.7) in such a manner that the mole ratio between the two

(the reaction ratio (a)/(b)), which were calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), would be 1/1.2. 0.5 wt.% (0.8 g), per the total of the fed reactants, of dibutyl tin oxide as a catalyst was fed and the mixture was reacted for esterification at $280^{\circ}\text{C} \pm 5^{\circ}\text{C}$ with nitrogen gas blown in. The synthesis product (No. 20 of Table 3) was obtained with AV = 1.1, OHV = 2.9, SV = 17.4, $\text{OHV}/(\text{SV} - \text{AV} + \text{OHV})$ of 0.15, $(\text{SV}^{**} - \text{AV}^{**} + \text{OHV}^{**})$ of 19.2, $(\text{SV}^{*} - \text{AV}^{*} + \text{OHV}^{*})$ of 14.1 and $(\text{SV}^{**} - \text{AV}^{**} + \text{OHV}^{**})/(\text{SV}^{*} - \text{AV}^{*} + \text{OHV}^{*})$ of 1.36. SV^{**} , AV^{**} , OHV^{**} , SV^{*} , AV^{*} and OHV^{*} are defined as follows: SV^{*} , AV^{*} and OHV^{*} are ideal values of SV, AV and OHV, respectively, after the reaction where one of (a) and (b), which is fed in the smaller moles than the other, has been completely consumed. SV^{**} , AV^{**} and OHV^{**} are ideal values of SV, AV and OHV, respectively, after the reaction has finished. As part of polyalkylenen oxide chains vaporizes in broken polyalkylenen oxide, $(\text{SV}^{**} - \text{AV}^{**} + \text{OHV}^{**}) / (\text{SV}^{*} - \text{AV}^{*} + \text{OHV}^{*})$ is getting larger. This is the reason the deinking agent of the invention is involved in such a difficulty. The value of $(\text{SV}^{**} - \text{AV}^{**} + \text{OHV}^{**}) / (\text{SV}^{*} - \text{AV}^{*} + \text{OHV}^{*})$ is preferably smaller than 1.25.

Production Example 2-6

No. 7 of Table 3 was obtained in the same way as Production Example 2-1 except that the reaction product (a1) and stearic acid (AV = 202.7) were fed in such a manner that the mole ratio between the two (the reaction ratio (a)/(b)), which were

calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), may be the same as the reaction rate shown in the table and esterification was effected at $250^{\circ}\text{C} \pm 5^{\circ}\text{C}$ with nitrogen gas blown in for 3 hours.

Production Example 2-7

Nos. 8 to 18, 22 and 23 of Table 3 was obtained by esterification in the same way as Production Example 2-1 except that the reaction product (a) was prepared in the same way as Production Example 2-1 and the reaction product (a) and a carboxylic acid (b) were fed at the reaction rate of (a)/(b) shown in the table.

No. 21 of Table 3 was obtained by mixing uniformly the reactants in the way where the mole ratio between the reaction product (a1) and stearic acid (AV = 202.7), which were calculated from the OHV of the reaction product (a1) and the AV of stearic acid (b1), may be 1/1.3.

Example 2

Deinking was effected with deinking agents of Table 3 in the same way as the deinking treatment of Example 1. Deinking performance was evaluated. Results are shown of Table 4. The flotation was effected with MT Flotator of Ishikawajima Sangyo Kikai Co., Ltd.

In evaluation of deinking agents, the pulp yield depends on foaming of the deinking agent. In addition, whiteness and ink collection greatly depend on the pulp yield. That is, the

smaller the pulp yield is, the higher the whiteness and the ink collection are. Among various deinking methods, some require a low foaming deinking agent, but some require a high foaming deinking agent. This is the reason the deinking effect can be difficultly compared between different pulp yields in terms of whiteness and ink collection. In the invention, the deinking effect is evaluated at a given pulp yield in terms of whiteness and ink collection, that is, a deinking efficiency. The evaluation is carried out at an added percentage of the deinking agent of 0.3 %. In No. 24 and No.25 a known ink removing agent was used in an amount of 0.2 wt.% and 0.3 wt.%, respectively, to the starting material.

Supposing a curve of the invention and another curve of No. 24 to 25, plotting pulp yields at the X axis and whiteness at the Y axis, starting at the pulp yield (100%) and whiteness before deinking, it is not considered that the two curves cross each other. This is the reason the deinking agent of the invention has a high deinking efficiency. No. 20 is inferior to the invention in view of deinking and is found to promote blacking. Then it is not good at handling.

Table 3

Deinking agent	Reaction product (a)				EO/PO Average number of moles added	AO Average number of moles added	Carboxylic acid (b)	(a)/(b) Reaction rate*1 (SV-AV+OHV)	OHV/ (SV-AV+OHV) *3	Esterification Reaction temperature °C	Reaction time Hour
		Material compound									
Test No.											
1	Production example 2-1	(a1)	Glycerin	EO210/PO90	300	(b1)	Stearic acid	0.77	0.20	225	4
2	↑	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.77	0.17	225	5
3	↑	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.77	0.08	225	6
4	Production example 2-2	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.77	0.41	215	4
5	↑	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.77	0.35	215	5
6	Production example 2-4	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.50	0.20	215	3
7	Production example 2-6	↑	Glycerin	EO210/PO90	300	↑	Stearic acid	0.83	0.12	250	3
8	Production example 2-7	(a2)	Glycerin	EO228/PO102	330	↑	Stearic acid	1.25	0.22	215	8
9	↑	(a3)	Glycerin	EO276/PO124	400	↑	Stearic acid	0.83	0.33	215	5
10	↑	(a4)	Glycerin	EO154/PO88	220	↑	Stearic acid	0.83	0.25	215	6
11	↑	(a5)	Glycerin	EO114/PO51	165	↑	Stearic acid	0.83	0.21	215	7
12	↑	(a6)	Glycerin	EO76/PO34	110	↑	Stearic acid	0.83	0.15	215	8
13	↑	(a7)	Glycerin	EO54/PO24	78	↑	Stearic acid	0.83	0.18	215	7
14	↑	(a8)	Glycerin	EO38/PO17	55	↑	Stearic acid	0.83	0.07	215	8
15	↑	(a9)	Glycerin	EO264/PO66	330	↑	Stearic acid	0.83	0.37	215	5
16	↑	(a10)	Glycerin	EO165/PO165	330	↑	Stearic acid	0.83	0.48	215	3
17	↑	(a11)	Glycerin	EO228/PO102	330	(b2)	Lauric acid	0.83	0.29	215	5
18	↑	(a12)	Glycerin	EO228/PO102	330	(b3)	Oleic acid	0.83	0.36	215	4
19	Production example 2-3		Tallow/ glycerin(1/0.2)	EO208/PO83	240*2	(b1)	Stearic acid	-	0.62	-	-
20	Production example 2-5	(a1)	Glycerin	EO210/PO90	300	↑	Stearic acid	0.83	0.15	280	1.5
21		(a1)	Glycerin	EO210/PO90	300	↑	Stearic acid	0.77	1.00	-	0
22	Production example 2-7	(a13)	Glycerin	EO28/PO12	40	(b1)	Stearic acid	0.83	0.34	215	6
23	↑	(a14)	Ethylene glycol	EO210/PO90	300	↑	Stearic acid	0.83	0.20	215	5
24			DI-767 (higher alcohol AO adduct, produced by Kao co.)								
25			DI-767 (higher alcohol AO adduct, produced by Kao Co.)								

*1: Reaction ratio (a)/(b) is a ratio of esterifying reaction, and is represented by the mole ratio between the (a) and the (b), calculated from the OHV of the (a) and the AV of the (b).

*2: The average number of AO molecules added to the glycerin skeleton.

*3: The OHV/(SV - AV + OHV) of each deinking agent

Table 4

Drinking agent Test No. of Table 3	Drinking agent addition ratio (%)	Whiteness (%)	Ink collecting property				Pulp yield (%)
			Remaining ink amount (ppm)		(II)-(I) difference	(I)	
			Completely washed sheet (I)	Drinking treatment sheet (II)			
1	0.3	47.7	302	810	508	83.9	
2	0.3	46.9	298	958	660	89.1	
3	0.3	45.9	302	1049	747	91.8	
4	0.3	48.1	307	788	481	78.7	
5	0.3	48.5	297	760	463	80.5	
6	0.3	47.7	303	811	508	85.3	
7	0.3	46.3	307	1027	720	89.4	
8	0.3	47.9	296	791	495	84.7	
9	0.3	48.4	298	767	469	82.5	
10	0.3	48.1	301	789	488	83.4	
11	0.3	47.8	299	814	515	86.0	
12	0.3	48.5	302	1004	702	89.8	
13	0.3	46.9	302	947	645	87.3	
14	0.3	45.9	310	1050	740	90.8	
15	0.3	48.4	312	779	467	78.8	
16	0.3	48.0	307	790	483	77.4	
17	0.3	47.6	305	823	518	82.2	
18	0.3	47.8	292	795	503	80.6	
19	0.3	46.9	311	973	662	73.1	
20	0.3	46.2	302	992	690	86.6	
21	0.3	46.6	297	981	684	72.0	
22	0.3	46.6	304	978	674	82.3	
23	0.3	46.7	303	918	615	82.1	
24	0.3	47.3	328	845	517	77.1	
25	0.2	46.9	317	887	570	80.3	